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(54) Method of bleaching cellulose pulp with ozone.

(57) The present invention relates to a method of bleaching cellulose pulp with ozone.

Ozone bleaching has been extensively studied in laboratory and pilot scale. It has been proved that at low consistencies, i.e. less than 5 %, ozone dissolves well in water and thus good transfer of substance between the ozone and the fibers in the water is achieved. On the other hand, it has been discovered that the ozone, being a gaseous substance, reacts well also directly with a fiber surface which, however, presupposes that the consistency of the suspension is over 25 %. Further, it has been discovered that in the intermediate rang between said consistencies ozone cannot satisfactorily contact the fibers. However, both environmental and pumping factors determine the operation to be carried out at that particular intermediate consistency range of 5 to 25 %.

A characteristic feature of the method of the present invention, which avoids the disadvantages of prior art methods and permits operation at the consistency range of 5 to 25 %, is that cellulose pulp is pumped with a high-consistency pump to a fluidizing mixer in which O_2/O_3 gas is introduced and mixed into the pulp so as to generate foam in which the fibers in the pulp and the ozone used as the bleaching agent are brought to contact with each other, and that the pulp is discharged from the mixer to a reaction vessel.

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Method of bleaching cellulose pulp with ozone

The present invention relates to a method of bleaching cellulose pulp with ozone.

Pulp for the paper and pulp industry must often be bleached in order to produce an end product of adequately high-quality. The most commonly used bleaching agents today are chlorine and oxygen. There is a tendency to avoid the use of chlorine or at least limit it to the minimum because of its damage to the environment. Oxygen is a good bleaching agent but its reaction selectivity is not always adequate whereby also other chemicals must be used. For these reasons, new bleaching agents have been sought. Ozone is one of these.

Ozone bleaching has been extensively studied in laboratory and pilot scale. Ozone has proved to be a good bleaching agent but also expensive and difficult to use as the consistency of the poulp to be bleached has to be very low or very high because of the high reactivity of the ozone. For example, at low consistencies, i.e. below 5 %, ozone is dissolved in the water and thus good transfer of mass between th ozone and the fibers in the water is achieved as the ozone containing water can freely flow between th fibers. It has also been found out that ozone, being a gaseous substance, reacts well directly with a dry fiber surface which presupposes that the consistency is so high, in most cases over 30 %, that there is practically no water on the surface of the fiber or between the fibers. Now the ozone containing gas can freely flow between the fibers.

On the other hand. for pumpability of the suspension. a certain amount of free water in the suspension must be accepted. For environmental and other reasons, it is resirable to keep this amount of water as small as possible. These factors define the range which is optimal for both the apparatus and th environment and lies between 5 and 25 %. However, ozone cannot contact the fibers in a satisfactory way in this particular consistency range as there is relatively little liquid in the suspension and it is bound in the spaces between the fibers and does not move freely in the suspension, and as ozone, being a gaseous substance, cannot move freely in the suspension because of the state of the suspension.

The problem described above has been solved in the method of the present invention the characterizing features of which are disclosed by the appended patent claims.

The invention provides a method for bleaching pulp with ozone at a consistency range of 5 to 25 %. According to the invention, conditions for good mass transfer are created even if gas or water cannot move freely in the suspension.

The invention is described below in detail with reference to the accompanying drawing figures of which

Fig. 1 illustrates a comparison of a state of the art ozone bleaching method and the ozone bleaching method of the present invention;

Fig. 2 illustrates a method according to a preferred embodiment for carrying out the ozone bleaching process of the invention; and

Fig. 3 illustrates another preferred embodiment of the ozone bleaching process.

Figure 1 illustrates, as a function of pulp consistency, comparative reaction results of a conventional ozone bleaching process and an ozone bleaching process applying the method of the present invention. In Fig. 1, curve A illustrates a typical result from ozone bleaching by a state of the art method. Curve B illustrates the result achieved by ozone bleaching with the method of the invention. By conventional methods at low consistencies (0 to 3 %) ozone dissolves in water and when the pulp-water mixture is agitated, good transfer of substance between the ozone and the fibers is achieved. Thus bleaching is effective in a dilute pulp suspension. At high conistencies (over 25 %) ozone bleaching is carried out mostly as gas phase bleaching. Ozone in gaseous form reacts well with a fiber surface whereby good transfer of substance is gained between the ozone and the fibers. Gas moves freely between the fibers and bleaching proceeds well. At the consistency range of 5 to 25 %, good ozone bleching requires special measures. The reason of the poor reaction is the somewhat solid nature of the pulp suspension at these consistencies. Water and air cannot readily move in the half-solid pulp. As illustrated by Fig. 1, curve B, the sam bleaching result as by conventional bleaching is achieved at both low and high consistencies by using the method of the invention.

A characteristic feature of the method of the invention is that in a pulp suspension of the consistency of 5 to 25 %, conditions are created where ozone can contact the fibers. The simplest way of doing this has proved to be the mixing of ozone gas into the fiber suspension with an intensive high-shear mixer so as to generated foam consisting of wood fibers, water and O_2/O_3 gas. The intense agitation required by the method can be generated by e.g. a fluidizing mixer disclosed in Finnish patent application no. 870747 by A. Ahlstrom Corporation. This mixer typically brings as much mixing efficiency to a small space that fibers or fiber bundles move loose from each other which results in good mixing of chemicals in the fiber

suspension. When gas is introduced to this kind of a mixing spac , foam is produced.

Table 1 presents the water and gas amounts used when ozone bleaching is performed at the consistency of 10 %. When the consistency is 10 % the pulp suspension contains one ton of fibers and nine tons of water. Approx. two tons of the water is absorbed in the walls of the fibers which leaves about seven tons of free water. The normal ozone dosage is around 1 %, i.e. 10 kg O_3. The concentration of the ozone gas is 10 % at the most, in other words the gas mixture contains 10 kg of O_3 and 90 kg of O_2 gas. As indicated by Table 1, the water/gas ratio varies between 1/10 and 1/1, depending on the pressure, which varies within the range 1 to 10 atm.

Table 1

1 ton fibers			
2 tons water in fibers			
7 tons free water	7 m^3	7 m^3	7 m^3
1 % O_3, 10 kg O_3, 90 kg 02	70 m^3	14 m^3	7 m^3
Pressure	1 bar	5 bar	10 bar
Water/gas ratio	1/10	1/2	1/1

The foam generated in a heavy-duty mixer is thus fairly light and the fiber material it contains makes the foam relatively stabile. There is a good transfer of substance between the gas the the fibers in the foam which gives a good bleaching result even though the gas or the water cannot freely move among the fibers.

Laboratory tests with a batch-type fluidizing mixer proved that large amounts of gas could be brought into the pulp suspensions. The tests were performed so that the gas and the pulp suspension wer intensively mixed for a short time (approx. 1 second) and then the bleaching reaction was allowed to happen without intensive mixing. The gas had, however, a tendency to separate, and therefore a b tter bleaching result in the laboratory batch mixer was achieved whem the gaseous chemicals first were intensively mixed into the fiber suspension in a fluidized state and the resulting gas-water-fiber foam or mixture was lightly agitated in order to prevent separation of gas.

Figure 2 illustrates one possible way of carrying out the ozone bleaching. Pulp 7 is pumped with a high-consistency pump 1 to an intensive mixer 2 into which ozone gas 5 is introduced. From the mixer, th pulp 7 is transferred to a reaction vessel 3 and therefrom to gas separation 4. After the reaction, residual gas 6, which is mainly the oxygen added to the pulp with the ozone 5, must be separated from the pulp. From the gas separation 4 the pulp flows on to further treatment. It is sometimes necessary to arrange light agitation in the reaction vessel 3 to prevent the foam or mixture formed in the mixer 2 from collapsing. The agitation can be accomplished by an agitator or by arranging proper flow conditions in the vessel 3.

Figure 3 illustrates an alternative ozone bleaching flow sheet with several ozone feed stages. The amount of the ozone to be introduced to the process may be so large that it is not advantageous to add all the gas at the same time. Then the method illustrated in Fig. 3 may be employed. Pulp 18 is pumped with a high-consistency pump 11 (preferably a fluidizing centrifugal pump by A. Ahlstrom Corporation) to a mix r 12 into which ozone 19 is introduced. Pulp 18 flows via reaction vessel 13 to a gas-removing high-consistency pump 14 (preferably a fluidizing, gas-separating centrifugal pump by A. Ahlstrom Corporation). Residual gas 21 is removed. From the high-consistency pump 14 the pulp flows to a second mixer 15, into which ozone 20 is introduced. After reaction 16 and gas removal 17 the pulp flows on for a further treatment stage. Again the reaction vessels 13 and 14 may be equipped with some kind of agitation.

It is clear that more than two bleaching stages can be carried out in the corresponding way. The stages can be pressurized, pressureless or performed at underpressure. The density of the produced foam can be regulated by choosing a desired pressure.

Pilot tests were performed according to a flow sheet corresponding to figure 2. Due to practical reasons it was not possible to use ozone gas but normal air. The goal of the tests was to study mixing of large amounts of gas into fiber suspensions. The reaction vessel 3 was partly replaced by a plexiglass pipe where the formed foam or mixture could be inspected. The foam or mixture varied much according to the surface tension of the water suspension, the type of fiber, and the amount of gas. In some tests the foam or mixture looked much like a snowstorm where bundles or fibres flew in a gas like snow flakes in air but in the gas there also fl w water drops and free single fibers. It is clear that high mixing int nsity is needed to form a foam or mixture like this from the original somewhat solid fiber suspension of the consistency of about 10 %. It is also clear that some light agitation or special fluid conditions are needed to prevent the

foam or mixture from collapsing. Other tests with soap added to reduce surface tension produced more milk-like foams.

The residual gas 6, 21, 22 produced by the reaction can be used in many ways. The typical ozone gas contains 9 parts oxygen per each part ozone. The residual gas is thus mainly oxygen as oxygen, because of its lower reactivity, does not have enough time to react. The residual oxygen gas can be used in any other stage of the pulp production process, for example as additional chemical elsewhere in the bleaching plant or as combustion gas e.g. in a soda recovery boiler or in a lime sludge reburning kiln.

Example 1

In a laboratory test, pulp was bleached with the sequence OZDED instead of the conventional OCEDED (O = oxygen, Z = ozone, E = alkaline extraction, D - chlorine dioxide). All bleaching stages were performed at the consistency of 10%. The goal was to verify that Z can replace CE and that the Z stage can be performed at the consistency of 10 %.

With an ozone dosage of about 0.9 %, the kappa number after the oxygen stage could be reduced to 8 - 9 in ozone stage without damaging the fibers. With a conventional CE stage, the kappa number is reduced to about 5 - 6 or somewhat lower than in the Z stage. However, the reduction in the Z stage is big enough to enable final bleaching with DED. It is thus possible to completely replace the chlorine with ozone by using medium consistency (10 %) ozone bleaching. This is a significant improvement as the severe environmental problems connected with chlorine are thus avoided.

The ozone stage performed at the consistency of 10 % was also compared with ozone stages performed at the consistencies of 1 % and 30 %. It turned out that ozone bleaching performed at the consistencies of 1 % and 10 % gave approximately the same result. This is probably due to good mass transfer in a very dilute agitated solution and in a foam-type mixture. The bleaching performed at the consistency of 30 % gave somewhat worse results. This is probably due to the fact that in a pulp of the consistency of 30 %, there are always fairly big flakes of fibers into the inside of which the ozone cannot reach properly, with the result that the surface of the falkes becomes overbleached and the inside unbleached.

Example 2

A mill feasibility study was performed to evaluate the size of the machinery needed for ozone bleaching at the consistencies of 1 %, 10 %, and 30 %.

At 1 %, a reaction vessel provided with agitation and operating at 1 % fiber-water suspension was needed into which oxygen-ozone gas was added. A residual gas collecting system was needed as well as a filter machine which after the bleaching raised the consistency of 10 - 15 % before the next process step.

At 10 %, only one mixer with high shearing capacity was needed, and a small reaction vessel with light agitation created by an agitator or flow conditions. No filter was needed but only a small gas separator before the next process step.

At 30 %, a press was needed before the reaction tower to raise the consistency. Additionally, a high-consistency mixer was needed, and a reaction tower capable of handling solid-gas reactions and provided with some type of intermediate bottoms. After the reaction tower, a dilution, gas separation and discharge system was needed.

It was obvious that the machinery needed for bleaching at the consistency of 10 % was by far the cheapest and simplest.

As can be comprehended from the above description, a new method avoiding the disadvantages of the prior art ozone bleaching methods has been developed. Only two preferred applications of the method have been described above which in no way intend to limit the invention from what has been presented in the appended patent claims which alone define the scope of protection and coverage of the invention. Thus, although only a few bleaching agents have been mentioned in the above examples, also the other bleaching stages may use an conceivable bleaching agent, e.g. chlorine, ozone, peroxid, chlorine dioxide, sodium hydroxide and enzymes.

Claims

1. A method of bleaching cellulose pulp with ozone, **characterized** in that the pulp is bleached in the form of a foam-like mixture at the consistency range of 5 to 25 %.

2. A method as claimed in claim 1, **characterised** in

- pumping the pulp with a medium consistency pump to a fluidizing mixer,
- feeding O_2/O_3 gas into the pulp therein,
- bringing the ozone serving as the bleaching agent in contact with the fibers of the pulp by means of mixing said gas into the pulp, and
- discharging the pulp from the mixer into a reaction vessel.

3. A method as claimed in claim 2, **characterized** in

- performing the bleaching in at least two steps such that
- residual gas is removed after the previous step in a reaction vessel, and
- additional O_2/O_3 gas is added in the mixer prior to the later step.

4. A method as claimed in claim 1, **characterized** in that the foam is a mixture of water, fibers, and O_2/O_3 gas.

5. A method as claimed in claim 1, **characterized** in

- mixing the O_2/O_3 gas into the pulp by a fluidizing mixer, whereby the foam-like mixture required by the bleaching reactions is produced.

6. A method as claimed in claim 2, **characterized** in

- separating the residual gas from the pulp after at least one bleaching stage.

7. A method as claimed in claim 3, **characterized** in

- separating the residual gas by a gas-removing pump used for pumping the pump for further treatment.

8. A method as claimed in claim 7, **characterized** in that the head produced by the second pump is low or negligible and the pump is used mainly for gas separation and the actual flow is kept up by a previuos pump.

9. A method as claimed in claim 3 or 6, **characterized** in that the residual gas is fed to another stage of the process, e.g. to serve as additional chemical in the bleaching plant or as combustion gas in a soda recovery boiler or a lime sludge reburning kiln.

10. A method as claimed in claim 7, **characterized** in

- introducing the pulp to another mixer after separating the gas therefrom,
- feeding O_2/O_3 gas into the pulp in said mixer,
- mixing said gas with the pulp so as to produce a mixture permitting the bleaching reaction between th ozone and the fibers, and
- discharging the pulp into a reaction vessel.

11. A method as claimed in claim 1 or 10, **characterized** in that the bleaching stages are pressurized, pressureless or performed at underpressure.

12. A method as claimed in claim 2, **characterized** in agitiating the pulp in a reaction vessel.

13. A method as claimed in claim 2, **characterized** in that the ozone bleaching stage is part of a larger bleaching plant where also the other bleaching stages are performed at a consistency of 5 to 25 %.

14. A method as claimed in claim 13, **characterized** in that the other bleaching stages use at least one of the following bleaching agents: chlorine, ozone, peroxid, chlorine dioxide, sodium hydroxide or enzymes.

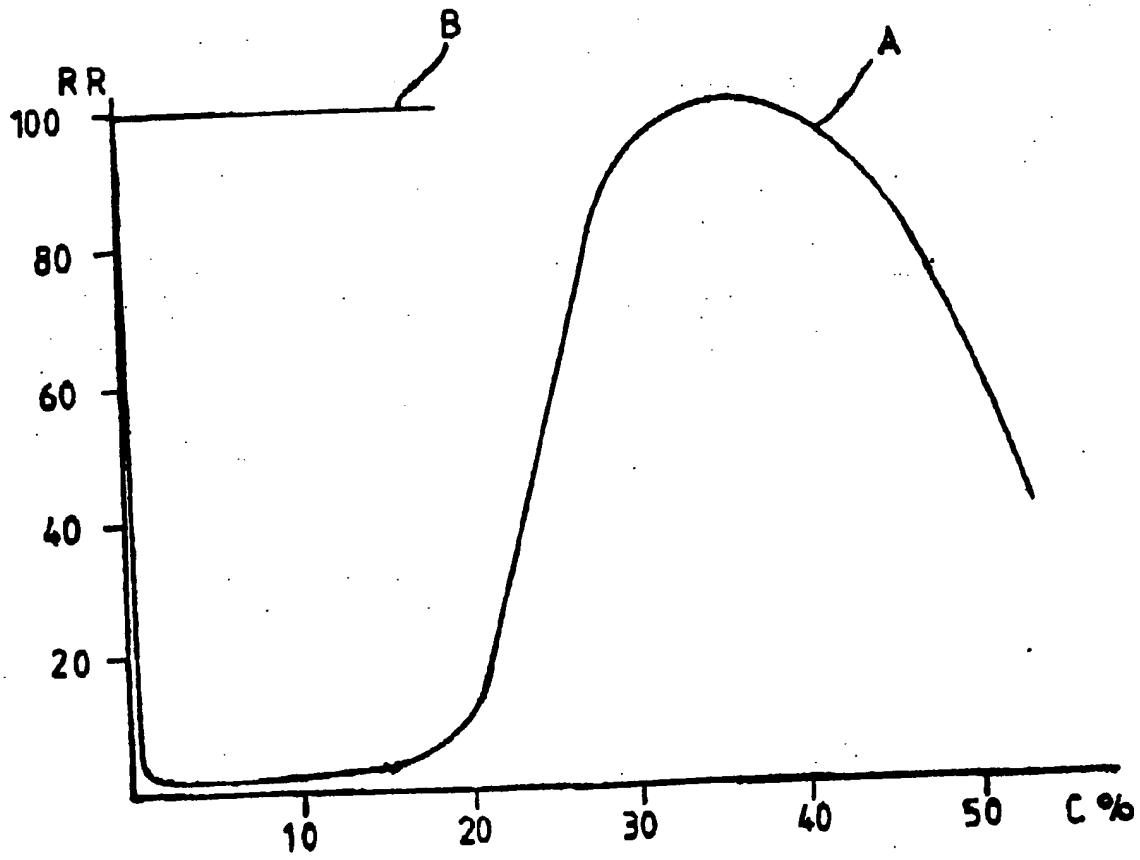

FIG. 1

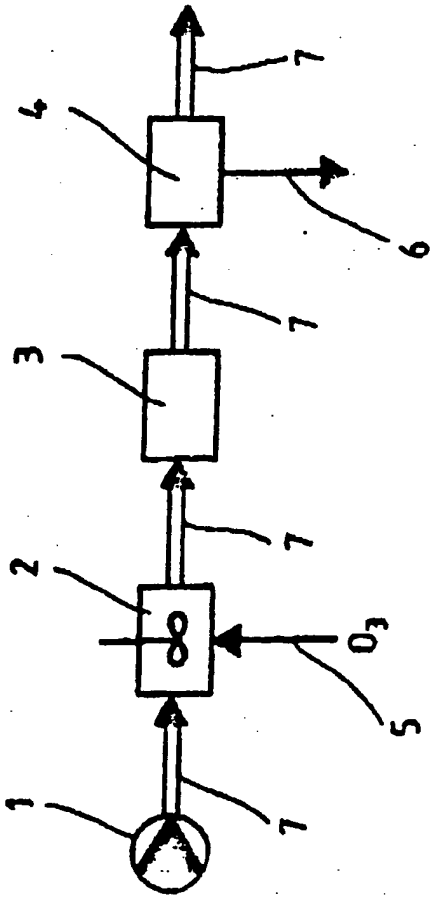

FIG.2

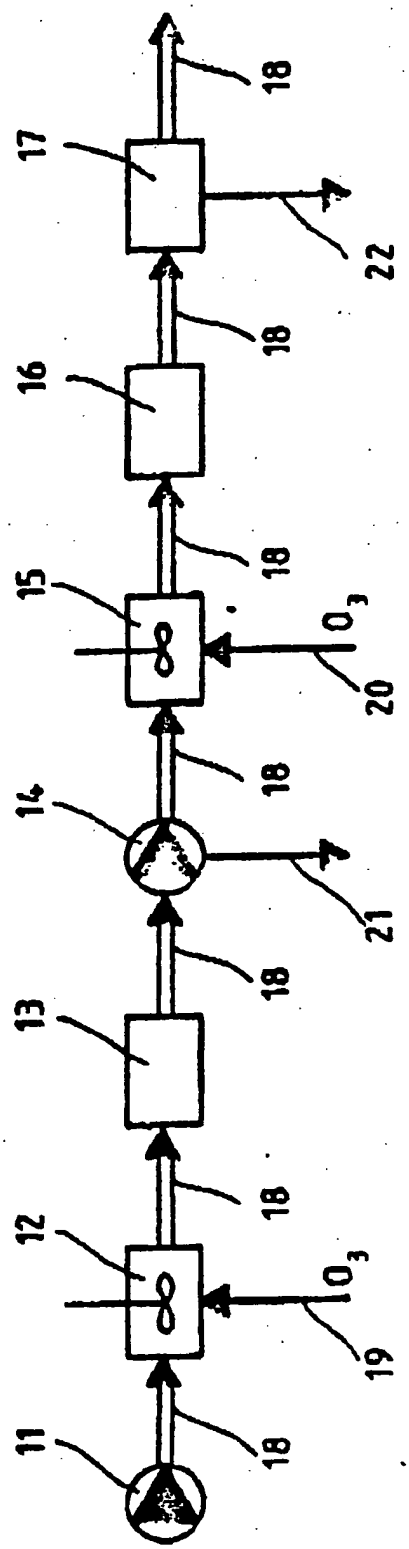

FIG.3

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(54) Method of bleaching cellulose pulp with ozone.

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A characteristic feature of the method of the present invention, which avoids the disadvantages of prior art methods and permits operation at the consistency range of 5 to 25 %, is that cellulose pulp is pumped with a high-consistency pump to a fluidizing mixer in which O_2/O_3 gas is introduced and mixed into the pulp so as to generate foam in which th fibers in the pulp and the ozone used as the bleaching agent are brought to contact with each other, and that the pulp is discharged from the mixer to a reaction vessel.

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EUROPEAN SEARCH REPORT

Application Number

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DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X,A	FR-A-2 353 674 (INTERNATIONAL PAPER COMPANY) * claims 1-6, 10-16 *	1,4,10-13	D 21 C 9/153 D 21 C 9/147
A	TAPPI JOURNAL. vol. 70, no. 11, November 1987, ATLANTA US pages 55 - 61; L. Tentch and S. Harper: "Oxygen-bleaching practices and benefits: an overview." * page 58, right-hand column, line 8 - page 60, right-hand column, line 6; figure 4 *	1-7,9, 11-13	
A	TAPPI JOURNAL. vol. 69, no. 7, July 1986, ATLANTA US pages 84 - 88; D.W. Reeve and P.F. Earl: "Mixing gases, water and pulp in bleaching." * the whole document *	1,4,5, 11-13	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

D 21 C

The present search report has been drawn up for all claims

Place of search	Date of completion of search	Examiner
The Hague	13 February 91	BERNARDO NORIEGA F.

CATEGORY OF CITED DOCUMENTS

X: particularly relevant if taken alone
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